

CHAPTER 1

Thermodynamics for Thermal Energy Storage

YULONG DING

Birmingham Centre for Energy Storage & School of Chemical Engineering,
University of Birmingham, Edgbaston, Birmingham B15 2TT, UK
Email: y.ding@bham.ac.uk

Thermodynamics is a science that deals with storage, transformation and transfer of energy. It is fundamental to the topics of thermal energy storage, which consists of a collection of technologies that store thermal (heat or cold) energy and use the stored energy directly or indirectly through energy-conversion processes when needed. Thermodynamics can be categorised into classical thermodynamics, statistical thermodynamics, chemical thermodynamics, equilibrium thermodynamics and non-equilibrium thermodynamics. This chapter introduces the classical thermodynamics concepts and laws considered to be most relevant to thermal energy storage. Attempts are made to relate these to thermal energy storage where appropriate.

1.1 Basic Concepts of Thermodynamics

Thermodynamics is a scientific discipline born in the 19th century to describe the operation of steam engines, which enabled the first industrial revolution that started in the UK and then spread around the

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world. It can be categorised into the following fundamentally related branches:¹

- *Classical thermodynamics*, developed in the 19th century, describes the states of a thermodynamic system at equilibrium using macroscopically measurable properties.
- *Statistical thermodynamics*, emerged in the late-19th century and early-20th century with the development of atomic and molecular theories, supplements the classical thermodynamics with an interpretation of the microscopic interactions and quantum-mechanical states.
- *Chemical thermodynamics* concerns the interrelation of energy with chemical reactions or with a physical change of state within the confines of the laws of thermodynamics.
- *Equilibrium thermodynamics* examines the transfer of matter and energy in a system or a body that, by its surroundings, can be driven from one state of thermodynamic equilibrium to another.
- *Non-equilibrium thermodynamics* deals with systems that are not in thermodynamic equilibrium.

1.1.1 Thermodynamic Systems, Surroundings and Control Volume

A thermal dynamic system is a device or combination of devices (*e.g.*, for energy storage) that contain a certain quantity of matter (*e.g.*, thermal energy storage materials). Anything outside the system is termed *surroundings*. The whole universe is made of the system and the surroundings. Systems have no mass exchange but can have energy exchange with the surroundings, and hence are termed closed systems or controlled-mass systems in some of the literature. A system with no energy exchange with surroundings is called an isolated system. A well thermally insulated thermal energy storage system can be regarded as an isolated system during its storage period.

Control volume refers to a volume in space into which, or from which, a substance flows. The control volume is also called an open system in some books. A thermal energy storage system can be regarded as a control volume or an open system during charge and discharge processes if the storage material also acts as a heat transfer fluid.

1.1.2 Phase

A phase refers to a quantity of matter that is homogeneous throughout. There are three phases in nature: gas, liquid and solid. A mixture of different phases is heterogeneous with a distinct macroscopic boundary between the phases. A sensible thermal energy storage material often exists as a single phase, whereas a latent heat storage material can be a single-phase (before or after phase change) or a two-phase mixture (during phase change).

1.1.3 Properties and State

A property is any quantity that serves to describe a system. Examples of thermodynamic properties are temperature and pressure. The state of a system refers to its condition as described by giving values to its properties at a particular instant. The features of thermodynamic properties are that they have unique values when the system is in a particular state, and the value does not depend on previous states that system has passed through; they are not a function of path and are therefore an exact differential:

$$\int_1^2 d\phi = \phi_2 - \phi_1 \quad (1.1)$$

where ϕ is a property; ϕ_1 is the property value at State 1 and ϕ_2 is the property value at State 2. There are two types of properties, intensive and extensive:

- *Intensive* properties do not depend on the mass of the system. Examples include temperature, pressure, specific volume and density.
- *Extensive* properties do depend on mass of the system. Mass and volume are examples of extensive properties.

The features of thermodynamic properties provide the basis for the development of methods for the calculation of important parameters such as energy-storage capacity, energy density and state-of-charge of thermal energy storage systems based on the property values during charge and discharge processes.

1.1.4 Thermodynamic Process, Cycle and Equilibrium

Thermodynamic equilibrium is the state of a system in which it is in mechanical, chemical and thermal equilibrium with no tendency for spontaneous change. This implies that all properties of a system at equilibrium have no tendency of change with time. A thermodynamic process refers to a path of successive states through which a system passes, whereas a quasi-equilibrium process refers to a process in which a system passing from one state to another deviates infinitesimally from equilibrium. A cycle is the process when a system experiences a series of quasi-equilibrium changes and returns to its initial state. A thermodynamic process is called isothermal, isobaric or isometric (or isochoric) if the process has a constant temperature, pressure or volume, respectively.

A typical thermal energy storage system is often operated in three steps: (1) charge when energy is in excess (and cheap), (2) storage when energy is stored with no demand and (3) discharge when energy is needed (and expensive). These three steps are called a process, and the three steps the system undergoes form a cycle if the state of the system returns to its initial

state. Most of the sensible heat storage processes, particularly those using solid materials, can be regarded as isobaric. Due to thermal expansion, the majority thermal energy storage processes are non-isometric. Isothermal processes occur during the phase change of latent heat storage systems and the storage step.

1.1.5 Pressure-Volume-Temperature (PVT) Behaviour of Pure Substances

Thermal energy storage processes often involve changes in temperature, volume and/or pressure. The relationship between these properties is therefore important for the design and operation of thermal energy storage systems. This subsection briefly discusses the pressure-volume-temperature (PVT) behaviour. The focus is on pure substances that have a homogeneous and invariable chemical composition and although they may exist in more than one phase, the chemical composition is the same in all phases. For example, a mixture of water, ice and steam is a pure substance, while a mixture of liquid air and gaseous air is not a pure substance. Sometimes, a mixture of gases, such as air, could be considered as a pure substance as long as there is no change of phase.

Figure 1.1 shows a schematic diagram illustrating how a PVT relationship is established. This involves heating a given mass of the pure substance under a given pressure and turning the material from solid to liquid and finally to the vapour phase. Plotting the volume as a function of temperature gives Figure 1.2 for the PVT at $P = P_1$.

Repeating the process at different pressures leads to the establishment of the PVT phase diagram as illustrated in Figure 1.3.

Figure 1.3 is of significance to thermal energy storage technologies in terms of materials selection, device design, integration and operation:

- Sensible heat storage operates mainly in single-phase regions, particularly the liquid- and solid-phase regions, although these operations in the gas-phase region can also occur;

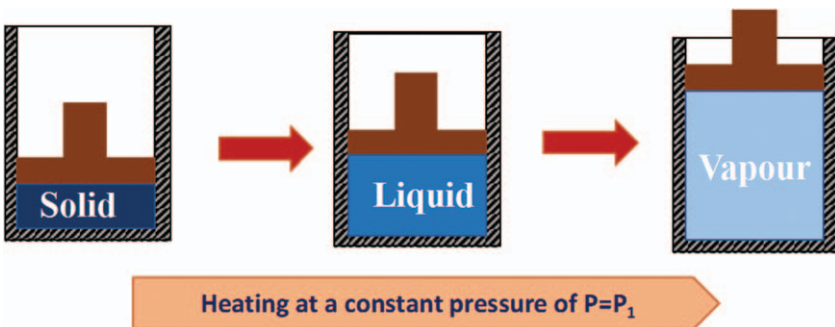


Figure 1.1 Establishment of PVT relationship for a pure substance.

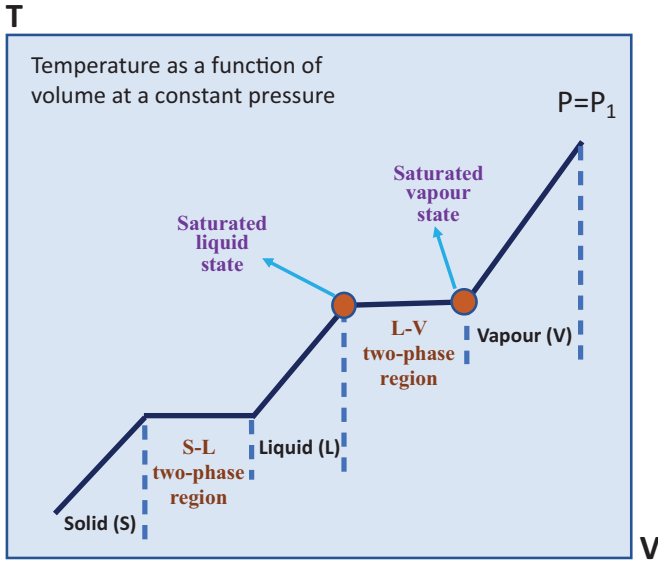


Figure 1.2 Temperature as a function of volume at a constant pressure $P = P_1$ for a pure substance.

- Latent heat storage operates mainly in the S-L two-phase region, though L-V operations have also been explored;
- Volume change as a function of temperature has to be considered when designing a thermal energy storage device as additional space allowance should be provided to account for expansion and contraction during charging and discharging processes.

As mentioned, there are thermal energy storage applications involving liquid-vapour (L-V) two-phase operations. For example, steam-based thermal energy storage using “steam accumulators” has been used in power plants for many years,² while oils-based thermal energy storage has been applied in concentrated solar power generation.³

Associated with the PVT behaviours are thermodynamic data tables that provide not only the relationship between P , V and T , but also include specific volume, internal energy, enthalpy and entropy measurements. The most popular data tables are steam tables and include a temperature entry, pressure entry, superheated vapour, water and compressed liquid water entries.^{1,4}

1.1.6 Equation of State

In the single-phase regions of the phase diagram illustrated in Figure 1.3, the temperature, pressure and volume may be related by the functional equation:

$$f(P, V, T) = 0 \tag{1.2}$$

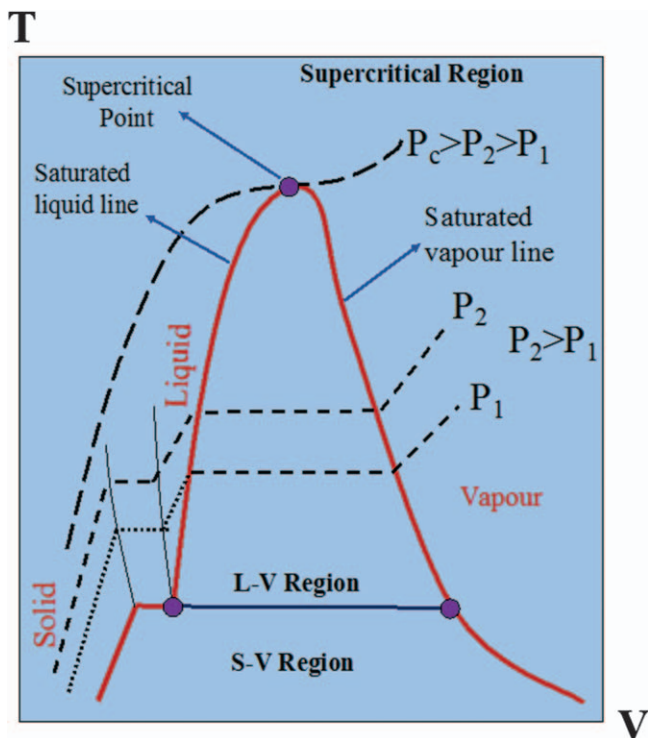


Figure 1.3 PVT behaviour of a pure substance.

This implies the existence of an equation of state relating the pressure, temperature and volume for any pure homogenous fluid in an equilibrium state. The simplest equation of state is the “ideal gas law” given by the equation:

$$PV = mRT \quad (1.3)$$

where m is the mass; and R is the gas constant, which relates to the gas molecular weight (M) by:

$$R = \mathbb{R}/M \quad (1.4)$$

with $\mathbb{R} = 8.314 \text{ kJ kg}^{-1} \text{ K}^{-1}$ in SI units. Eqn (1.3) applies to the low-pressure and high-temperature regions of Figure 1.3. At high pressures and/or low temperatures, eqn (1.3) deviates from reality and a parameter called compressibility is defined:

$$Z = PV/(mRT) \quad (1.5)$$

with $Z=1$ for the ideal gases. Figure 1.4 illustrates how Z changes with pressure and temperature for nitrogen, which, together with eqn (1.5) can be used to determine the PVT relationship.

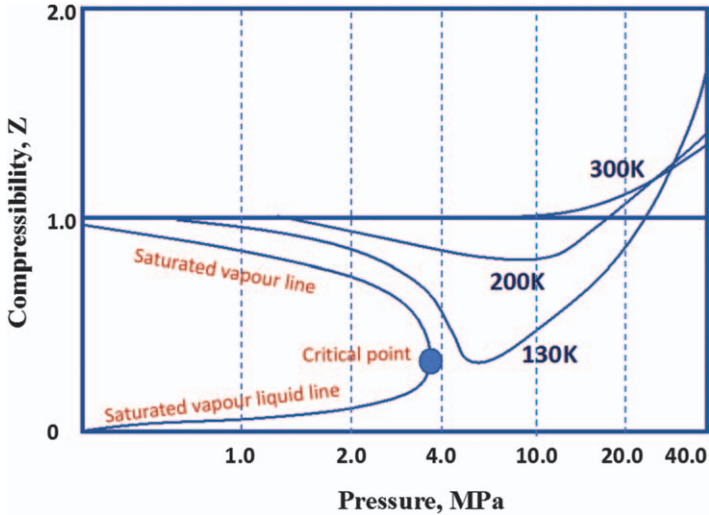


Figure 1.4 Compressibility of non-ideal gases.

1.1.7 Multicomponent Systems

So far, the discussion has been on pure substances. Thermal energy storage systems and thermal energy systems often involve the use of mixtures or multicomponent fluids and/or composition changes due to, for example, chemical reactions. An example of this is thermochemical thermal energy storage.

Multicomponent systems can be broadly divided into two categories, namely ideal and non-ideal mixtures. For ideal gas mixtures, two models have been proposed, the Dalton model and the Amgat model. These models assume that the behaviour of each of the components behaves like an ideal gas and is not affected by the presence of other components.⁵ For non-ideal mixtures, a new class of thermodynamic properties, known as partial properties, is needed to develop the fundamental property relationships for these cases. This will not be discussed further and interested readers are referred to references on chemical thermodynamics.⁴

1.2 Thermodynamic Laws

1.2.1 The First Law of Thermodynamics

The introduction of the first law of thermodynamics requires the definition of two parameters, work and heat.

- Work, denoted as W , is an energy form that is transferred by a system to its surroundings by a mechanism through which the system can spontaneously exert macroscopic forces on its surroundings. Through the same mechanisms, energy can transfer from the surroundings to

the system. There is a sign convention for work in physics, which may be different in other scientific disciplines, such energy transfer is counted as a positive amount of work done by the system on its surroundings. A related concept, power, is often used in thermal energy storage and is defined as the time rate of doing work.

- Heat, denoted as Q , is another form of energy transferred across a system boundary at a given temperature to another system or surroundings at a lower temperature through conduction, convection or thermal radiation. There is also a sign convention in physics that the energy transfer is counted as positive heat transferred to the system. A related concept is the “adiabatic system”, which is defined as $Q = 0$.

Heat and work both have a unit of J (Joules) under the SI convention. It is important to note that heat and work are not thermodynamic properties. They depend on the process the system undergoes and are therefore path functions.

The first law of thermodynamics is essentially an equation of conservation of energy, which, for a system undergoing a cycle, takes the form:

$$J \cdot \oint \delta Q = \oint \delta W \quad (1.6)$$

where $\oint \delta Q$ is cyclic integral of heat, implying physically the net heat transfer during the cycle; $\oint \delta W$ is the cyclic integral of work, meaning physically the net work during the cycle; and J is the proportionality factor that depends on units of Q and W , and is 1 in SI units. Note that the use of δQ and δW is to denote non-exact differentials as Q and W are not properties. Eqn (1.6) states that the cyclic integral of the heat is proportional to the cyclic integration of the work, which is observed from numerous experimental observations.

Application of eqn (1.6) to a cycle, starting from State 1 and returning to State 1 *via* State 2 through different paths of A and B, is easy to show by using the equation:

$$\int_1^2 (\delta Q - \delta W)[\text{Path A}] = \int_1^2 (\delta Q - \delta W)[\text{Path B}] \quad (1.7)$$

Eqn (1.7) implies that, although heat and work are path functions, their difference, $\delta Q - \delta W$, does not depend on the path and is therefore a property. This property is defined as energy, denoted by dE in thermodynamics:

$$dE = \delta Q - \delta W \quad (1.8)$$

This is an alternative form of the first law of thermodynamics. Integration of eqn (1.8) between State 1 and State 2 gives:

$$Q_{1-2} = E_2 - E_1 + W_{1-2} \quad (1.9)$$

where Q_{1-2} and W_{1-2} refer to heat and work, respectively, due to the change between State 1 and State 2; E_1 and E_2 are energy at State 1 and State 2, respectively. As energy consists of (macroscopic) kinetic energy, KE ;

(macroscopic) potential energy, PE ; and (microscopic) internal energy, U ; where U includes chemical energy, energy associated with atoms and molecules, and other forms of energy, it can be determined by the equation:

$$E = U + KE + PE \tag{1.10}$$

Inserting eqn (1.10) into eqn (1.9) gives:

$$Q_{1-2} - W_{1-2} = U_2 - U_1 + KE_2 - KE_1 + PE_2 - PE_1 \tag{1.11}$$

where KE and PE can be given, respectively, by:

$$KE = \frac{1}{2} mV^2 \tag{1.12}$$

$$PE = mgz \tag{1.13}$$

with m being the mass; V the speed and z the elevation. Combining eqn (1.12) and (1.13) with eqn (1.11), one has:

$$Q_{1-2} = U_2 - U_1 + \frac{1}{2} m(V_2^2 - V_1^2) + mg(z_2 - z_1) + W_{1-2} \tag{1.14}$$

Eqn (1.14) has been commonly used in engineering applications. The internal energy, U , is a thermodynamic property that is a function of temperature, pressure and volume. As temperature, pressure and volume are related *via* the equation of state as discussed in Section 1.1.6, the following holds for U :

$$U = U(T, V) \quad \text{or} \quad u = u(T, v) \tag{1.15}$$

where u and v are specific internal energy and specific volume, respectively. Differentiation of eqn (1.15) using the specific properties gives:

$$du = \left(\frac{\partial u}{\partial T} \right)_v dT + \left(\frac{\partial u}{\partial v} \right)_T dv \tag{1.16}$$

For constant volume processes, eqn (1.16) reduces to:

$$du = \left(\frac{\partial u}{\partial T} \right)_v dT \tag{1.17}$$

If one defines c_v as the specific heat under constant volume conditions, one gets:

$$c_v = \left(\frac{\partial u}{\partial T} \right)_v \tag{1.18}$$

Eqn (1.17) becomes:

$$du = c_v dT \quad \text{or} \quad u_2 - u_1 = \int_{T_1}^{T_2} c_v dT \tag{1.19}$$

One can then calculate the internal energy once the c_v is available. There is a database for the c_p ; refer to the thermodynamic data tables discussed in Section 1.1.5. Many industrial processes including thermal energy storage systems are operated under constant-pressure conditions. In thermal energy storage systems, another thermodynamic parameter termed enthalpy is often used and is defined as:

$$H = H(T, P) \quad \text{or} \quad h = h(T, P) \quad (1.20)$$

where H and h are enthalpy and specific enthalpy, respectively. Differentiation of eqn (1.20) using the specific properties gives:

$$dh = \left(\frac{\partial h}{\partial T} \right)_P dT + \left(\frac{\partial h}{\partial P} \right)_T dP \quad (1.21)$$

For constant pressure processes, eqn (1.21) reduces to:

$$dh = \left(\frac{\partial h}{\partial T} \right)_P dT \quad (1.22)$$

If one defines c_p as the specific heat under constant pressure conditions, one gets:

$$c_p = \left(\frac{\partial h}{\partial T} \right)_P \quad (1.23)$$

Eqn (1.22) becomes:

$$dh = c_p dT \quad \text{or} \quad h_2 - h_1 = \int_{T_1}^{T_2} c_p dT \quad (1.24)$$

Data tables are available in the literature for c_p (see Section 1.1.5). An inspection of eqn (1.20) and (1.23) shows that the specific heat implies the amount of heat required to bring up the temperature of a unit amount of material by 1K under either constant-volume or constant-pressure conditions. It is therefore highly relevant to thermal energy storage, particularly for sensible heat storage.

1.2.2 The Second Law of Thermodynamics

As discussed in Section 1.2.1, the first law of thermodynamics states that during any cycle that a system undergoes, the cyclic integral of heat is equal to cyclic integral of work. However, it does not determine whether or not a process will actually occur. This question is answered by the second law of thermodynamics, which states that a process proceeds in a certain direction. To discuss the second law in detail, two concepts are introduced:

- **Heat engines:** A heat engine is a device that operates in a thermodynamic cycle and does a certain amount of net-positive work through the transfer of heat from a high-temperature body to a low-temperature body. The thermal efficiency of the heat engine is defined as the ratio of the energy sought (the net-positive work) to the energy costs (the total heat transferred from the high-temperature body).
- **Heat pumps (refrigerators):** A heat pump is a device that operates in a cycle that requires work, and that accomplishes the objective of transferring heat from a low-temperature body to a high-temperature body. The efficiency of the heat pump is defined as the ratio of the energy sought (the heat transferred out of the low-temperature body) to the energy costs (the amount of work input). This efficiency is often called the coefficient of performance.

With these two concepts, we can discuss the second law of thermodynamics, which is given by the following two classical statements:

- **The Kelvin–Planck statement:** It is impossible to construct a heat engine that operates in a cycle that receives a given amount of heat from a high-temperature source and does an equal amount of work;
- **The Clausius statement:** It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a cooler body to a hotter body.

These two statements imply that it is impossible to build a heat engine with a thermal efficiency of $\eta = 100\%$ or to construct a refrigerator that operates without work input. The question is then: what would be the maximum efficiency for these devices? This leads to the definition of reversible processes. A reversible process is a process that once having occurred can be reversed and in doing so, leaves no changes in either system or surroundings. A cycle made of reversible processes has the highest efficiency. Such a cycle is often called Carnot cycle and the efficiency of the cycle depends on the temperatures of the low (T_L) and high (T_H) heat sources:

$$\eta = 1 - \frac{T_L}{T_H} \quad \text{for heat engines} \quad (1.25a)$$

$$\eta = \frac{1}{\left(\frac{T_H}{T_L}\right) - 1} \quad \text{for heat pumps} \quad (1.25b)$$

Eqn (1.25a, b) set the theoretical upper limits for heat engines and heat pumps, respectively. The assessment of the actual efficiencies and ways to enhance efficiencies require the understanding of the loss mechanisms and quantification of the losses. We also need to understand the criteria for the direction of processes. These are discussed next.

The inequality of Clausius: Consider a heat engine operated between a high-temperature reservoir (T_H) and a low-temperature reservoir (T_L); one can find the following:

$$\oint \delta Q \geq 0 \quad \text{and} \quad \oint \frac{\delta Q}{T} \leq 0 \tag{1.26}$$

The equality holds for reversible cycles. The consideration of a heat pump will lead to the same inequality as eqn (1.26).

Entropy: Consider two reversible cycles, 1A2B1 and 1C2B1, as illustrated in Figure 1.5, the application of the Clausius inequality gives:

$$\oint \frac{\delta Q}{T} = 0 = \int_1^2 \left(\frac{\delta Q}{T}\right)_A + \int_2^1 \left(\frac{\delta Q}{T}\right)_B \tag{1.27}$$

$$\oint \frac{\delta Q}{T} = 0 = \int_1^2 \left(\frac{\delta Q}{T}\right)_C + \int_2^1 \left(\frac{\delta Q}{T}\right)_B \tag{1.28}$$

Comparison of eqn (1.27) and (1.28) gives:

$$\int_1^2 \left(\frac{\delta Q}{T}\right)_A = \int_1^2 \left(\frac{\delta Q}{T}\right)_C \tag{1.29}$$

This implies that $\int \frac{\delta Q}{T}$ is the same for all reversible paths between States 1 and 2. In other words, this quantity is independent of path and is therefore a property of a system. This property is called entropy, denoted as S :

$$dS = \left(\frac{\delta Q}{T}\right)_{\text{rev}} \tag{1.30}$$

S has a unit of kJ K^{-1} , defined by using reversible processes. As entropy is a property, it does not depend on the path, and the calculation of entropy can be done through assumed reversible processes. The importance of the

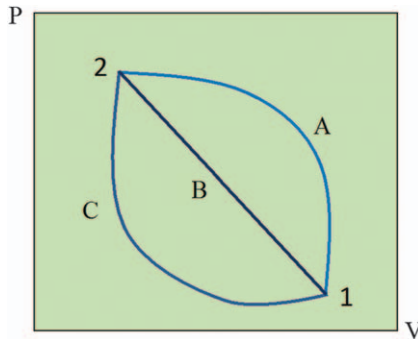


Figure 1.5 Definition of entropy.

concept *entropy* in the second law is synonymous with the concept of energy in the first law of thermodynamics.

Consider Figure 1.5 further, if 1A2 and 2B1 are reversible but 1C2 is irreversible, one has the following two equations, respectively, for 1A2B1 and 1C2B1:

$$\oint \frac{\delta Q}{T} = \int_1^2 \left(\frac{\delta Q}{T} \right)_A + \int_2^1 \left(\frac{\delta Q}{T} \right)_B = 0 \tag{1.31}$$

$$\oint \frac{\delta Q}{T} = \int_1^2 \left(\frac{\delta Q}{T} \right)_C + \int_2^1 \left(\frac{\delta Q}{T} \right)_B < 0 \tag{1.32}$$

Combining eqn (1.31) and (1.33) gives:

$$\int_1^2 \left(\frac{\delta Q}{T} \right)_A > \int_1^2 \left(\frac{\delta Q}{T} \right)_C \tag{1.33}$$

As Path A is reversible and entropy is a property, one has:

$$\int_1^2 \left(\frac{\delta Q}{T} \right)_A = \int_1^2 dS_A = \int_1^2 dS_C \tag{1.34}$$

As a result, the following stands:

$$\int_1^2 dS_C > \int_1^2 \left(\frac{\delta Q}{T} \right)_C \tag{1.35}$$

Given the Path C was arbitrary, generalisation of the eqn (1.35) gives:

$$dS \geq \frac{\delta Q}{T} \quad \text{or} \quad S_2 - S_1 \geq \int_1^2 \frac{\delta Q}{T} \tag{1.36}$$

The equality in eqn (1.36) corresponds to reversible processes, whereas the inequality corresponds to irreversible processes. Eqn (1.36) is one of most important equations in thermodynamics, which states the influence of irreversibility on entropy of systems, namely, irreversibilities increase the entropy of the system. It can also be used to check whether a process would occur.

Consider a system and its surroundings, which constitute the whole universe, as defined in Section 1.1.1, it is easy to show the following:

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \geq 0 \tag{1.37}$$

This implies that the entropy of the universe consisting of entropy of the system and its surroundings either increases or remains constant. If the system exchanges work or heat with its surroundings, it is possible to have

$\Delta S_{\text{system}} < 0$, but then entropy of its surroundings will have to increase such that $\Delta S_{\text{universe}} \geq 0$.

The second law given by eqn (1.36) can be rewritten as:

$$dS = \frac{\delta Q}{T} + \delta S_{\text{gen}} \quad (1.38)$$

where $\delta S_{\text{gen}} \geq 0$ denotes entropy generation. The rate of entropy change can then be given by:

$$\frac{dS}{dt} = \frac{\delta Q/\delta t}{T} + \delta S_{\text{gen}}/\delta t \quad (1.39)$$

Eqn (1.39) implies that the change in the entropy is due to flux of entropy into the system due to heat transfer, and entropy generation due to irreversibilities. Eqn (1.39) can be applied to a control volume to give an entropy balance equation, which, in combination with the mass balance and energy balance (the first law), have been used extensively in engineering design and modelling of energy devices and systems including thermal energy storage systems.⁶⁻⁸

1.3 Concluding Remarks

In this chapter, some definitions, concepts and associated physical meanings and laws of classical thermodynamics are introduced. The focus is on those which are highly relevant to thermal energy storage. Explicit attempts have been made to relate the definitions, concepts and laws of thermodynamics to thermal energy storage technologies.

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